164425

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SAS Number

SPECIAL ANALYTICAL SERVICES

Client Request

✓ Regional Transmittal ____ Telephone Request

A. EPA Region/Client: III Chuck Kanetsky

B. RSCC Representative: Colleen K. Walling

C. Telephone Number: FTS 922-3752 or (301) 224-2740

D. Date of Request: 9-18-87

E. Site Name: Nozenski Junkyard Red Clay Creek, PA/DE

Please provide below description of your request for Special Analytical Services under the Contract Laboratory Program. In order to most efficiently obtain laboratory capability for your request, please address the following considerations, if applicable. Incomplete or erroneous information may result in a delay in the processing of your request. Please continue response on additional sheets, or attach supplementary information as needed.

1. General description of analytical service requested:
2,3,7,8-TCDD analysis with 1.0 -2.0 ppt detection limit of sediments and fish. Total tetra thru octa dioxin/furan isomers and each of the 2,3,7,8-substituted dioxin/furan isomers.

2. Definition and number of work units involved (specify whether whole samples or fractions; whether organics or inorganics; whether aqueous or soil and sediments; and whether low, medium or high concentration):
12 sediment samples

3. Purpose of analysis (specify whether Superfund (enforcement or remedial action), RCRA, NPDES, etc.):
Superfund TTFA03N922

4. Estimated date(s) of collection:
September 22, 1987

5. Estimated date(s) and method of shipment:
upon SAS award by Federal Express

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6. Number of days analysis and data required after laboratory receipt of samples:
30 - days

7. Analytical protocol required (attach copy if other than a protocol currently used in this program):
Sediment/soil sample are to be anzlyzed by soxhlet extraction as per EPA 600/4-86-004 "Protocol for the Analysis of 2,3,7,8-Tetrachlorodibenzo-p-Dioxin by high-resolution gas chromatography/high-resolution mass spectrometry.

Any method deviations must be approved by Region III prior to bid award. Copies of methods used must accompany the data package.

8. Special technical instructions (if outside protocol requirements, specify compound names, CAS numbers, detection limits, etc.):
Total tetra thru octa dioxin/furan analysis shall be performed by high resolution GS/MS using procedures approximating the Region VII, November 1985 protocols for LRMS. For specific 2,3,7,8-X isomer analysis a labeled internal standard for each isomer is desired (subject to availability).

Specific isomer analysis are to be calculated from the column providing the most specificity for that isomer. All specific isomer samples must be run on DB-5 or on SP-2330/CPsil1-88 equivalents. All analysis on SP 2330/CPsil1-88 must meet CLP performance check mixture criteria before analysis proceeds and at the end of each day or every 12 hours - which ever is more frequent. Instrument calibration minimal requirements:

a. 2,3,7,8-TCDD as per protocol. All other based on three point calibration curve with all response factors within 20% of the average RF.

b. Validation of the current ins'rument response by obtaining RF within 20% of the previously obtained average RF before analysis proceeds each day and at the end of each day or every 12 hours which ever is more frequent.

9. Analytical results required (if known, specify format for data sheets, QA/QC reports, Chain-of-Custody documentation, etc.) If not completed, format of results will be left to program discretion.
All 2,3,7,8-TCDD results are to be reported in the CLP format as per IFB WA84-A002. All total isomer and specific 2,3,7,8-X isomer analysis are to be reported non-2,3,7,8-X isomers
Also see Appendix II.

10. Other (use additional sheets or attach supplementary information, as needed):
Three QA containers supplied.

11. Name of sampling/shipping contact:
Charles Kanthesz 215/597-9176

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12. Data Requirements:

Parameter	Detection Limit	Precision desired (+% or concentration
2,3,7,8-TCDD	1-2 ppt	
other isomers to be analyzed under conditions which give 2,3,7,8-TCDD a 1 ppt detection limit.		

13. QC Requirements:

Audits Required	Frequency of Audits	Limits (Percent or Concentration)
37 Cl 2,3,7,8-TCDD surrogate	every sample	>60% - <140% recovery
Matrix spike	1 per batch*	>60% - <140% recovery
In-house duplicate	1 per batch*	<30% RPD
Method blank	1 per batch*	<1 ppt 2,3,7,8-TCDD

*batch = 24 samples of same matrix.

14. Action Required if Limits are Exceeded:
Re-extraction and/or reanalysis if any internal standard is not measured with signal to noise >10:1.

Please return this request to the Sample Management Office as soon as possible to expedite processing of your request for special analytical services. Should you have any questions or need any assistance, please contact your Regional representative at the Sample Management Office.

15. Request prepared by [signature] 9/17/87

16. Request reviewed by: Calvin K. Walling (CKW)
Date: 9-18-87

DELIVERABLES REQUIRED FOR HRGC/LRMS DIOXIN/FURAN ANALYSIS

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I. SAMPLE PREPARATION AND METHOD DOCUMENTATION

A. "Cookbook" style step-by-step method including instrument/conditions, type and source of reagents.

B. Analyst bench record describing dilutions, weighings and any unusual occurrences during prep, extraction or clean up.

C. Calculations and method used in determination of percent solids (where applicable).

II. DIOXIN/FURAN QUANTITATION AND IDENTIFICATION DOCUMENTATION

A. Identification of CDDs and CDFs to be established according to Table III.

B. Provide estimated detection limits for all analytes not reported as positive, adhering to the following suggested requirements for adaption of procedures from the IFB for 2,3,7,8-TCDD:

1. NOISE LEVEL: It is preferrable to average the noise level using peak height as opposed to peak area. Peak area may be used only if a representative average area can be chosen with integration endpoints approximately as many scans wide as the peak width of the nearest internal standard (measured at 25% of its peak height).

2. PEAKS SLIGHTLY OUTSIDE CRITERIA: Whenever peaks above 2.5 times noise level for both ions maximize simultaneously, and ion ratios are outside ±15% of theoretical, but within ±25% of theoretical, any and all interferences of this type within the retention time window must be summed together for inclusion in the reported detection limit.

3. MULTIPLE INTERFERENCES: Whenever one third or more of the retention time window for identification of a congener class is obscurred or overlapped by peaks above 2.5 times the noise level for both ions which maximize simultaneously, but with ion ratios outside ±15% of theoretical, then the detection limit calculation must account for these interferences (as opposed to being based upon the noise level of cleaner regions of the chromatogram).

C. Example calculation of sample result(s).

D. Chromatograms to be supplied for each standard, blank, sample, and QC sample in the order specified in Section IV., paragraph C.

E. List of exact ion masses monitored for each isomer/class, current and historical response factors and relative retention times for positive ID

F. TICs for all samples and QC (including blanks).

G. Document any altered calculations due to the presence of interferences. (Examples: When the M+4 ion of a C_{13}PCDF is interferred by the molecular ion of a PCDD, quantitation involving the C_{13}PCDF would be based upon the M+2 ion.)

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QUALITY CONTROL

A. All positive method blank contents labelled on TICs and possible sources explained.

B. Surrogate accuracy data in tabular form; (concentration used, amount detected and percent accuracy).

C. Date and source of standard used to verify all in-house standards used for quantitation (include SICs/TICs) where applicable.

D. Daily column chromatography checks SICs and TICs (i.e., mixture of 5-7 dioxin/furan isomers that elute near 2,3,7,8).

E. Detection limit calculations.

F. Results of internally prepared spiked samples, duplicates, including SICs and TICs. NOTE: One matrix spike and duplicate required for soils and one MS and dup. for water samples.

IV. ORDER OF DELIVERABLES

General comment: Use EPA identification on all report sheets and chromatograms.

A. Case Narrative - include summary of problems, list of samples reported in package and any chain-of-custody information.

B. QC Summary:
Form B-1
Summary Form for other surrogates in Format similar to Form B-1.

C. Sample Data Grouped BY SAMPLE in ascending order (based on EPA identification number). NOTE: Reagent blanks precede samples.

1. Summary of Sample Results
2. Raw data for analysis on DB-5 column
Order with suggested ions.
Simultaneous display of SICs:
a) TCDD m/z 322, 328, 332, 334
b) TCDD m/z 257, 320, 322, 332, 334
c) PeCDD m/z 356, 358, 368, 370
d) HxCDD m/z 390, 392, 402, 404
e) HpCDD m/z 424, 426, 436, 438
f) OCDD m/z 458, 460, 470, 472
g) TCDF m/z 304, 306, 316, 318, 374, or 376
h) PeCDF m/z 340, 342, 352, 354, 408, or 410
i) HxCDF m/z 374, 376, 386, 388, 444 or 446
j) HpCDF m/z 408, 410, 420, 422, 478 or 480
k) OCDF m/z 442, 444, 454, 456 512

NOTE: Include in-house worksheets which show ion ratios for all peaks or note ratios on SICs. Integrated area and peak height must be supplied for all peaks 2.5 times above background. If this information is not printed on SICs, then supply a computer-generated list immediately behind the relevant SIC.

3. Raw data for analysis on SP-2331 column, order as above. (Red)
NOTE: Include in-house worksheets which show ion ratios for all peaks or note ratios on SICs. Integrated area and peak height must be supplied for all peaks 2.5 times above background. If this information is not printed on SICs, then supply a computer-generated list immediately behind the relevant SIC.

C. Standards Raw Data Group BY INSTRUMENT

1. For DB-5 column:

a) Initial Calibration
Include worksheets which show ion ratios for all standards.

b) Continuing Calibration (in order of chronology)
Include % difference calculation and worksheet which show ion ratios for all standards.

2. For SP2331 column: For those samples requiring confirmation of 2,3,7,8-substituted isomers:

a) Initial Calibration (for those sample sets which require work as per IFB):

1) Form B-2
2) Raw Data

b) Continuing Calibration (in order of chronology)

1) Form B-3
2) Raw Data

E. Other Relevant Information

1. Percent moisture calculations

2. Run log

3. Notes from analyst notebooks

4. Extraction log

5. Any other information requested as SAS deliverable

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TABLE I

DETECTION LIMITS FOR CDDs AND CDFs

Total TCDDs $\leq$ 0.1 ppb

Total PeCDDs $\leq$ 0.5 ppb

Total HxCDDs $\leq$ 2.5 ppb

Total HpCDDs $\leq$ 100.0 ppb

Total TCDFs $\leq$ 1.0 ppb

Total PeCDFs $\leq$ 1.0 ppb

Total HxCDFs $\leq$ 10.0 ppb

Total HpCDFs $\leq$ 100.0 ppb

TABLE II

PCDD AND PCDF CONGENERS FOR DEFINING THE GC WINDOWS FOR EACH HOMOLOGUE ON A DB-5 COLUMN

PCDD - Positional Isomer		No. of Chlorines	PCDF - Positional Isomer	
Early Eluter	Late Eluter		Early Eluter	Late Eluter
1,3,6,8	1,2,8,9	4	1,3,6,8	1,2,8,9
1,2,4,7,8	1,2,3,8,9	5	1,3,4,6,8	1,2,3,8,9
1,2,3,4,6,8	1,2,3,4,6,7	6	1,2,3,4,6,8	1,2,3,4,8,9
1,2,3,4,6,7,8	1,2,3,4,6,7,9	7	1,2,3,4,6,7,8	1,2,3,4,7,8,9
12346789		8	12346789	

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Date: 7/10/86

TABLE III

CRITERIA FOR IDENTIFICATION OF CDDs AND CDFs

For a gas chromatographic peak to be identified as a CDD or CDF, it must meet these criteria:

1. The signal to noise (S/N) ratio for all monitored ions must be greater than 2.5.

2. The monitored ions must maximize within three scans of each other.

3. The ratio of the intensities of the two largest ions in the molecular ion isotope cluster must be within 15% of the theoretical value.

4. For non-2,3,7,8-isomers, the RT must be between the RTs of the earliest and latest eluting compounds of that group, as verified by retention time marker solutions.

5. For 2,3,7,8-substituted isomers, the RRT must be within 0.06 of the RRT of an authentic standard run on the same day. Chromatographic separation of 2,3,7,8-isomers from their closest eluting isomers should be documented, if possible.

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Table IV

Suggested Abbreviation and GC/MS Quantitation Ions
for Polychlorinated-Dibenzodioxins (PCDD)

Compound	Abbreviation	Quantitation ions A and B (m/z) for analyte	Quantitation ions C and D (m/z) for $^{13}C12$ labeled internal standard
Tetrachloro-DD	TCDD	A 319.8965 B 321.8936	C 331.9368 D 333.9339
Pentachloro-DD	PeCDD	A 355.8546 B 357.8516	C 367.8949 D 369.8919
Hexachloro-DD	HxCDD	A 389.8156 B 391.8127	C 401.8559 D 403.8530
Heptachloro-DD	HpCDD	A 423.7766 B 425.7737	C 435.8169 D 437.8140
Octachloro-DD	OCDD	A 457.7377 B 459.7347	C 469.7780 D 471.7750

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Table V

Suggested Abbreviation and GC/MS Quantitation Ions for Polychlorinated-Dibenzofurans (PCDF)

Compound	Abbreviation	Quantitation ions A and B (m/z) for analyte	Quantitation ions C and D (m/z) for $^{13}C_{12}$ labeled internal standard
Tetrachloro-DF	TCDF	A 303.9016 B 305.8987	C 315.9419 D 317.9390
Pentachloro-DF	PeCDF	A 339.8597 B 341.8567	C 351.9000 D 353.8970
Hexachloro-DF	HxCDF	A 373.8207 B 375.8178	C 385.8610 D 387.8581
Heptachloro-DF	HpCDF	A 407.7817 B 409.7788	C 419.7831 D 421.8191
Octachloro-DF	OCDF	A 441.7428 B 443.7398	C 453.7831 D 455.7801